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Conversion of a Hydrido−Butenylcarbyne Complex to η^2-Allene-Coordinated Complexes and Metallabenzenes

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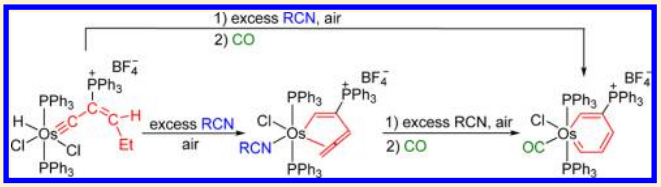
Supporting Information

ABSTRACT: Treatment of $OsCl_2(PPh_3)_3$ with HC≡CCH(OH)Et produces the cyclic complex $Os(PPh_3)_2Cl_2(CHC(PPh_3)CH(OH)CH_2CH_3)$ (**1**), which can undergo dehydration to give the hydrido−alkenylvinylidene complex $Os(PPh_3)_2HCl_2(=C=C(PPh_3)CH=CHCH_3)$ (**2**). Reaction of **2** with HBF_4 generates the hydrido−butenylcarbyne complex $[OsHCl_2(\equiv CC(PPh_3)=CH(Et))(PPh_3)_2]BF_4$ (**3**).



The complex **3** evolves into the unstable metallabenzene $[(PPh_3)_2(RCN)ClOs(CHC(PPh_3)CHCHCH)]BF_4$ (**4**; RCN = benzonitrile, 2-cyanobenzaldehyde, 3-methoxyacrylonitrile, 2-cyanoacetamide) via triple hydrogen eliminations in the presence of excess nitriles in refluxing $CHCl_3$ in an air atmosphere. The ligand substitution reaction of **4** with excess CO affords the stable metallabenzene product $[(PPh_3)_2(CO)ClOs(CHC(PPh_3)CHCHCH)]BF_4$ (**5**). The key intermediates, η^2-allene-coordinated osmium complexes $[(PPh_3)_2(RCN)ClOs(CH=C(PPh_3)CH=C=CH_2)]BF_4$ (**6**; RCN = benzonitrile, 2-cyanobenzaldehyde, 3-methoxyacrylonitrile, 2-cyanoacetamide) can be captured by performing the conversion at room temperature. Remarkably, in the absence of nitriles, reaction of **3** with excess CO only generates the vinylethenyl complex $[(PPh_3)_2(CO)_2ClOs(CH=C(PPh_3)CH=CHCH_3)]BF_4$ (**7**). The complexes **1**−**3**, **5**, **6a**, and **7** have been structurally characterized by single-crystal X-ray diffraction. Detailed mechanisms of the conversions have been investigated with the aid of density functional theory (DFT) calculations. DFT calculations suggest that the high stablility of the carbonyl coordinated complexes in the conversion inhibits the further transformation to metallabenzene product. However, the transformation is both kinetically and thermodynamically favorable in the presence of the relatively weaker nitrile ligand, which is consistent with the experimental conversion of **3** to **5** via unstable metallabenzenes **4** observed for in situ NMR experiments.

INTRODUCTION

Transition-metal complexes with a metal−carbon triple bond or a metal−carbon double bond, namely, carbyne or carbene complexes, have attracted considerable attention because they can display unique properties and mediate various reactions to construct unsaturated molecules.[1] Metalla-aromatics can be regarded as a special organometallic species containing a carbyne or carbene segment, which is derived from replacement of a (hydro)carbon unit in aromatic hydrocarbons with a transition-metal fragment.[2] As one of the major issues of metalla-aromatic chemistry, the isolation and characterization of stable metallabenzenes have been extensively investigated. It is now well established that the synthesis of metallabenzenes can be achieved by means of the reactions of simple transition-metal complexes with unsaturated hydrocarbons[3] and the conversions of various unsaturated metallacycles.[4] In our previous study (Chart 1), we found that the hydrido−vinylcarbyne complex $[OsHCl_2(\equiv CC(PPh_3)=CHPh)(PPh_3)_2]BF_4$ could undergo formal [4 + 2] cycloaddition with acetonitrile to form the metallapyridine and intramolecular C−H activation of the phenyl ring to form the metallanaphthalene and metallanaphthalyne.[5] These observations prompted us to synthesize other carbyne complexes to construct new metallacycles. In this paper, we report the synthesis of the hydrido−butenylcarbyne complex $[OsHCl_2(\equiv CC(PPh_3)=CH(Et))(PPh_3)_2]BF_4$ (**3**) and its conversions to η^2-allene-coordinated complexes and metallabenzenes via triple-hydrogen eliminations. Detailed mechanisms of the conversions have been investigated with the aid of density functional theory (DFT) calculations.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Hydrido−Alkenylvinylidene Complex $Os(PPh_3)_2HCl_2(=C=C(PPh_3)CH=CHCH_3)$ (2) and the Hydrido−Butenylcarbyne Complex $[Os(PPh_3)_2HCl_2(\equiv CC(PPh_3)=CHCH_2CH_3)]BF_4$ (3). Treatment of $OsCl_2(PPh_3)_3$ with 1.3 equiv of CH≡CCH(OH)Et in tetrahydrofuran led to the formation of the corresponding osmacyclic complex **1**, which can be isolated as a yellow solid in 60% yield (Scheme 1). Complex **1** has been characterized by multinuclear NMR spectroscopy and elemental analysis. The structure has been further determined by single-crystal X-ray diffraction. Selected bond lengths and angles are given in Table 1. The crystallographic details are given in Table S1 (Supporting

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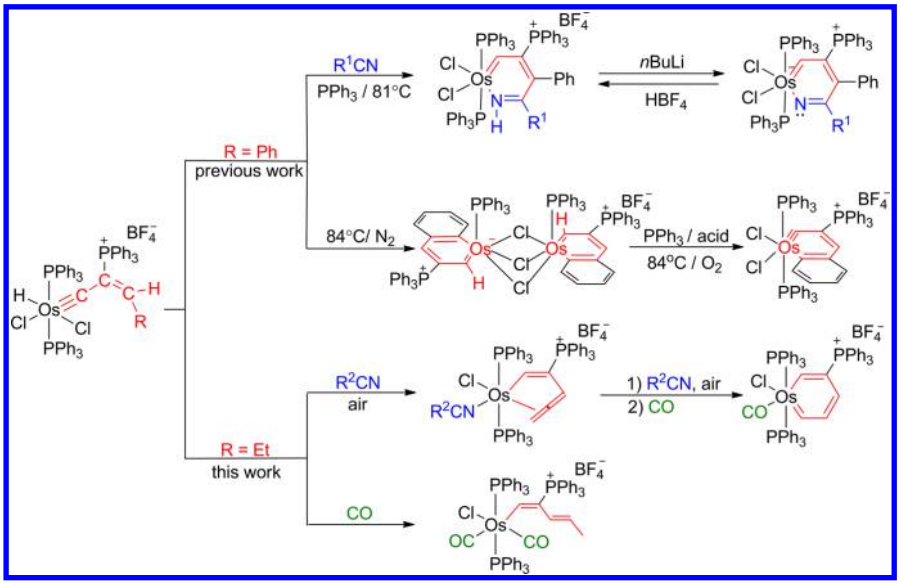
Chart 1



Scheme 1. Formation of Complexes 2 and 3

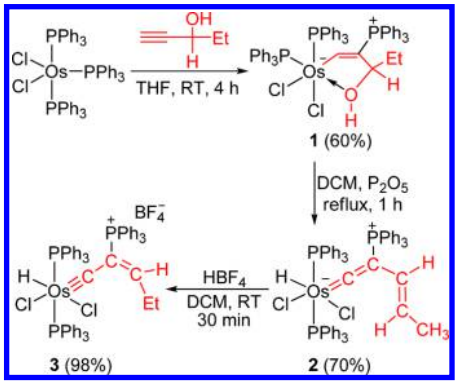


Table 1. Selected Bond Lengths and Angles for 1−3

	1	2	3
	Bond Lengths (Å)		
Os1−C1	1.983(10)	1.762(8)	1.721(4)
C1−C2	1.389(14)	1.406(11)	1.445(6)
C2−C3	1.522(14)	1.482(12)	1.349(6)
C3−C4	1.522(16)	1.319(13)	1.493(6)
C4−C5	1.50(2)	1.495(13)	1.531(6)
C3−O1	1.438(13)		
	Bond Angles (deg)		
Os1−C1−C2	118.3(8)	179.1(7)	179.6(4)
C1−C2−C3	120.4(9)	121.9(7)	121.5(4)
C2−C3−C4	115.9(9)	125.7(9)	125.2(4)
C3−C4−C5	112.5(12)	122.7(10)	112.5(4)
C2−C3−O1	107.0(8)		
C3−O1−Os1	116.3(6)		

Information). The molecular structure of **1** is shown in Figure 1, which confirms that the hydroxyl group is coordinated to the metal center through the lone pair of electrons on the oxygen atom. The structural features associated with the five-membered metallacycle are similar to those of $[OsCHC(PPh_3)CH(Ph)(OH)]Cl_2(PPh_3)_2$.[5b]

When a suspension of complex **1** and excess P_2O_5 in CH_2Cl_2 was stirred under reflux for 1 h, a yellow solution was produced,

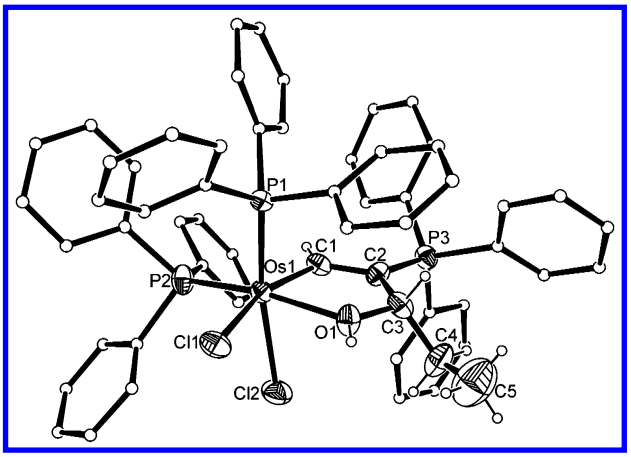


Figure 1. X-ray molecular structure for the cation of complex **1** drawn with 50% probability ellipsoids. The hydrogen atoms in the PPh_3 groups are omitted for clarity.

from which complex **2** was isolated in about 70% yield. Due to its poor solubility in ordinary organic solvents, attempts to obtain a full NMR spectroscopic characterization of complex **2** failed. Fortunately, after recrystallization of the crude product from CH_2Cl_2/Et_2O, a single crystal of **2** was obtained, making it possible to determine its solid-state structure. The crystallographic details are given in Table S1 (Supporting Information). Selected bond lengths and angles are given in Table 1. The X-ray diffraction study reveals that **2** is a hydrido−alkenylvinylidene complex (Figure 2). The Os1−C1 (1.762(8) Å) and C1−C2 (1.406(11) Å) bond lengths compare well with those found in other osmium−vinylidene complexes.[6] The Os1−C1−C2 bond angle of 179.1(7)° shows almost linear geometry. The C−C separations along the C5 chain (C1−C2 = 1.406(11) Å, C2−C3 = 1.482(12) Å, C3−C4 = 1.319(13) Å, and C4−C5 = 1.495(13) Å) agree well with $C(sp^2)=C(sp^2)$ double, $C(sp^2)-C(sp^2)$ single, $C(sp^2)=C(sp^2)$ double, and $C(sp^2)-C(sp^3)$ single bonds, respectively. In addition, high-resolution mass spectroscopy of complex **2** shows a peak at m/z 1079.2496, which is consistent with the suppositional formula. On the basis of the characterized structures and the experimental conditions,

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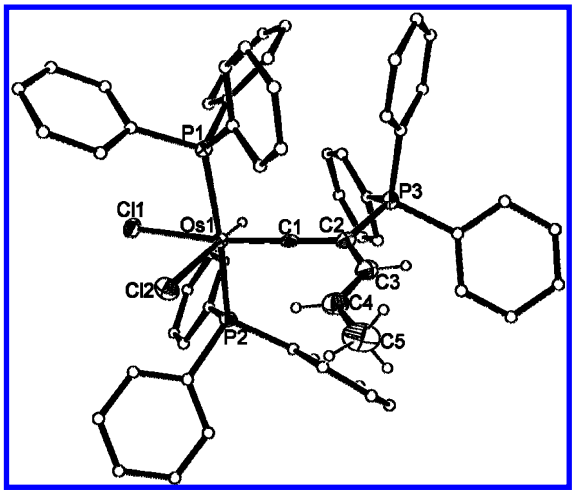

Figure 2. X-ray molecular structure for the cation of complex **2** drawn with 50% probability ellipsoids. The hydrogen atoms in the PPh_3 groups are omitted for clarity.

we speculated that the formation of **2** may proceed through α-hydride migration followed by dehydration.

Complex **2** is stable both in the solid state and in solution at room temperature, and it can tolerate weak alkali in solution. However, it is very reactive toward acid. In the presence of HBF_4, complex **2** readily converted to complex **3** in CH_2Cl_2 in high yield. Actually, the formation of **3** can also be detected by directly treating complex **1** with HBF_4 under reflux. However, it was difficult to separate complex **3** from the reaction mixture because the reaction is not clean and **3** is not stable under these reaction conditions. Complex **3** can tolerate acids but is reactive to alkalis. As monitored by in situ NMR spectroscopy, **3** can convert to **2** in the presence of alkalis such as MeONa or NaOH.

The molecular structure of **3** has also been unambiguously confirmed by X-ray diffraction (Figure 3). The X-ray diffraction

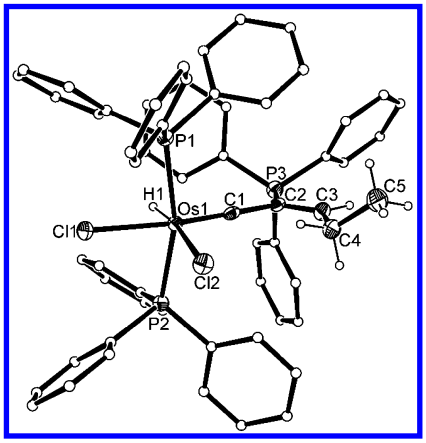

Figure 3. X-ray molecular structure for the cation of complex **3** drawn with 50% probability ellipsoids. The counteranion and hydrogen atoms in PPh_3 groups are omitted for clarity.

study demonstrates that **3** has a distorted-octahedral geometry around the metal center, with the phosphine ligands occupying trans positions. The perpendicular plane is formed by the two *cis*-disposed chloride ligands, the hydride ligand, and the carbyne group. The Os1−C1 bond length of 1.721(4) Å is within the range of those reported for typical triple bonds of osmium carbyne complexes.[7] Similar to the case for most previously reported alkenylcarbyne complexes,[8] the carbyne unit of **3** displays good linearity, as reflected by the Os1−C1−C2 angle of 179.6(4)°. In addition, the characteristic spectroscopic data of **3** are consistent with the structure shown in Figure 3.

Reactions of Hydrido−Butenylcarbyne Complex 3 with Nitriles: Formation and Characterization of Metallabenzenes. It is known that the electron richness of the metal center would impede the 1,2-hydrogen shift from the metal to the carbyne carbon atom. Esteruelas et al. had previously demonstrated with DFT calculations and kinetic studies the influence of the coligands on the activation parameters of the 1,2-hydrogen shift.[9] Hence, we first attempted to modify this hydrido−butenylcarbyne complex **3** with a less electron rich metal center by a ligand substitution reaction. When the reaction of **3** with benzonitrile was performed in $CHCl_3$ at reflux temperature for 1 h, complex **4a** was identified by in situ NMR, instead of the expected substitution product (Scheme 2). Unfortunately, the reaction is not clean and our attempts to obtain a pure sample of **4a** from the crude products failed, as complex **4a** is unstable in solution. The ^1H NMR spectrum of the crude products from the reaction of **3** with benzonitrile showed two characteristic ^1H signals at 18.9 (d, J(HH) = 7.3 Hz) and 16.3 (d, J(PH) = 24.8 Hz) ppm. The two signals are assignable to the two OsCH groups in **4a**, as the chemical shifts of the two signals are similar to those of OsCH of our previously reported benzonitrile-monosubstituted osmabenzene $[Os(CHC(PPh_3)C(CH_3)CHCH)Cl(C_6H_5CN)(PPh_3)_2]$-$BPh_4$.[10] In agreement with the presence of **4a** in the mixture, the mass spectrum showed an ion peak at m/z 1180.3, corresponding to $[Os(CHC(PPh_3)CHCHCH)Cl(C_6H_5CN)$-$(PPh_3)_2]^+$. In addition, we obtained the carbonyl-substituted product of **4a**, i.e. complex **5**, which is structurally similar to **4a** (vide infra).

To isolate other stable metallabenzene products, we carried out analogous reactions by using different nitriles. However, we only observed similar results, as monitored by in situ NMR spectroscopy. The relative metallabenzene products $[Os(CHC$-$(PPh_3)CHCHCH)Cl(RCN)(PPh_3)_2]BF_4$ (RCN = 2-cyanobenzaldehyde (**4b**), 3-methoxyacrylonitrile (**4c**), 2-cyanoacetamide (**4d**)) are all unstable. Similarly, the ^1H NMR spectra of the crude products from the reactions of **3** with other nitriles also showed two characteristic ^1H signals (19.3 (d, J(HH) = 7.1 Hz), 16.1 (d, J(PH) = 24.2 Hz) ppm, **4b**; 19.0 (d, J(HH) = 7.2 Hz), 16.4 (d, J(PH) = 23.2 Hz) ppm, **4c**; 19.4 (d, J(HH) = 6.2 Hz), 16.5 (d, J(PH) = 23.1 Hz) ppm, **4d**), assignable to the two OsCH groups of $[Os(CHC(PPh_3)CHCHCH)Cl(RCN)$-$(PPh_3)_2]BF_4$.

In this context, we then carried out ligand substitution reactions to convert these unstable complexes **4** to more stable species. After the mixture of **3** and excess nitriles in $CHCl_3$ was stirred at reflux temperature for 1 h, a continuous stream/flow of CO was bubbled through the solution, which was further stirred for 0.5 h at room temperature to give a brown solution. The carbonyl-monosubstituted osmabenzene complex **5** could be isolated as a purple solid from the reaction mixture. The osmabenzene complex **5** has been characterized by multinuclear NMR spectroscopy and high-resolution mass spectroscopy. In the ^1H NMR spectrum, the two downfield signals of Os*CH* appear at 15.9 and 13.1 ppm. The ^{31}P NMR spectrum shows two singlet peaks at −2.9 (Os*P*Ph_3) and 18.6 (*CP*Ph_3) ppm. As complex **5** has good solubility in organic solvents, it is difficult

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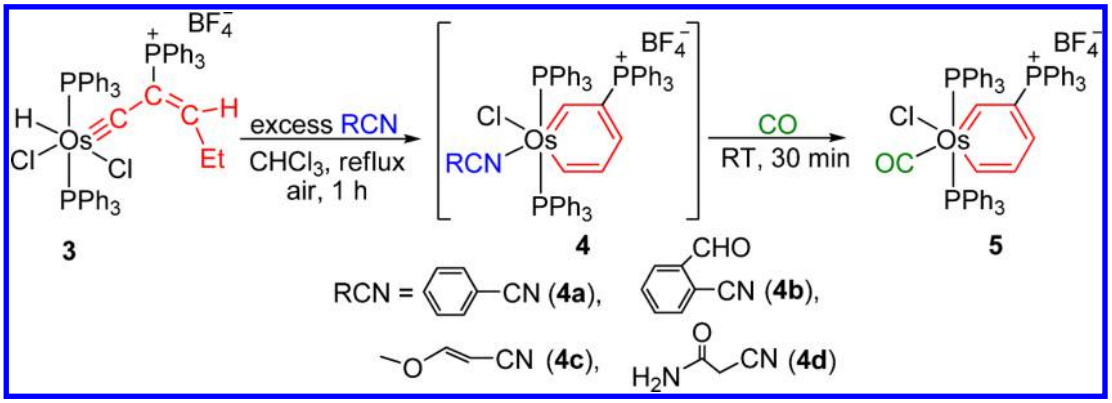
Scheme 2. Conversion of Complex 3 to Metallabenzenes 4 and 5



to obtain a single crystal of **5** to determine its solid-state structure. Fortunately, the counteranion BF_4^- in **5** can be easily replaced with BPh_4^- by treatment of **5** with $NaBPh_4$ to give osmabenzene **5′**. The structure of **5′** was confirmed unambiguously by X-ray diffraction. The crystallographic details are given in Table S1 (Supporting Information). The molecular structure of **5′** is shown in Figure 4, which reveals that it is a

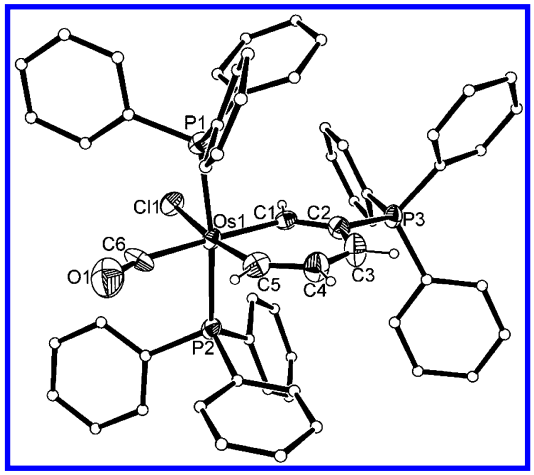


Figure 4. Molecular structure for compound **5′** (50% probability ellipsoids). The counteranion and hydrogen atoms in PPh_3 groups are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1−C1 = 2.080(7), Os1−C5 = 1.929(8), C1−C2 = 1.361(10), C2−C3 = 1.443(11), C3−C4 = 1.386(12), C4−C5 = 1.349(12); C1−Os1−C5 = 86.1(3), C2−C1−Os1 = 130.2(6), C1−C2−C3 = 122.8(7), C2−C3−C4 = 123.4(8), C3−C4−C5 = 124.0(8), C4−C5−Os1 = 133.4(7).

metallabenzene complex formed via replacing the RCN ligand in **4** by one carbonyl ligand. The six-membered metallabenzene ring of **5′** displays good coplanarity. The mean deviation from the least-squares plane through Os1 and C1−C5 is 0.0109 Å, and the sum of angles in the six-membered ring is 719.9°, which is very close to the ideal value of 720°. The C−C bond distances of the C1−C5 chain in the range of 1.349(12)−1.443(11) Å and the lack of significant alternations in the C−C bond distances suggest that **5′** has a delocalized structure.

Mechanistic Considerations for the Conversion of 3 to 5. In order to understand the mechanistic aspects for the reactions of **3** with nitriles, we initially undertook the same experiments at room temperature to trap the intermediates of the reactions. As shown in Scheme 3, when a solution of **3** and excess benzonitrile in $CHCl_3$ was stirred at room temperature for 5 h, **3** was completely consumed to give **6a** as the dominant product.

Complex **6a** was isolated as a yellow solid. It has been characterized by elemental analysis and multinuclear NMR spectroscopy as well as single-crystal X-ray diffraction analysis. The crystallographic details are given in Table S1 (Supporting Information). A view of the complex cation is shown in Figure 5. The X-ray diffraction study indicates that **6a** contains a conjugated osmacycle with a terminal double bond of an allene coordinated to the metal atom. As a consequence of its coordination to the metal center, the allene unit is strongly bent with a C3−C4−C5 angle of 159.8°. In agreement with the structure, the ^{31}P NMR spectrum displays signals at δ −9.9 (s, Os*P*Ph_3) and 8.8 (s, *CP*Ph_3) ppm, respectively. The ^1H NMR spectrum shows the Os*CH* signal at δ 11.5 ppm, the *CH*CCH_2 signal at δ 7.6 ppm (obscured by the phenyl signals and confirmed by $^1H-^{13}C$ HMBC), and the $CHCCH_2$ signal at δ 2.8 ppm. In the ^{13}C NMR spectrum, the signals of OsCH and *C*PPh_3 appear at δ 203.4 and 120.9 ppm, while the three carbon signals of the coordinated allene backbone are observed at δ 116.8 ($CHCCH_2$), 190.3 ($CHCCH_2$), and 26.0 ($CHCCH_2$) ppm, respectively.

Further study shows that other analogous intermediates can be captured from the reactions of **3** with other nitriles. Thus, the η^2-allene-coordinated osmium complex **6b** was obtained by starting from **3** and 2-formylbenzonitrile (Scheme 3), which was isolated as a yellow solid. Similarly, the 3-methoxyacrylonitrile-containing complex **6c** and 2-cyanoacetamide-containing complex **6d** were obtained by starting from **3** with 3-methoxyacrylonitrile or 2-cyanoacetamide, which were also isolated as yellow solids (Scheme 3).

Experimentally, the η^2-allene-coordinated osmium complexes **6** can be converted to the final osmabenzene product **5**, providing strong evidence for **6** as the key intermediates for the reactions. When a mixture of **6** and excess nitriles in $CHCl_3$ was stirred at reflux temperature for about 1 h and then excess CO was bubbled into the mixture, the expected complex **5** was isolated (Scheme 3). It is interesting that the conversion of **6** to **5** does not occur in the absence of excess nitriles even when we increase the reaction temperature to 60 °C, as indicated by in situ NMR.

On the basis of the characterized structure of the complexes **6** and the reaction conditions, we conjectured that the weak coordination ability of nitriles may play an important role in the conversion of hydrido−butenylcarbyne complex **3** to metallabenzene **5**. To test this idea, we carried out the reaction of **3**

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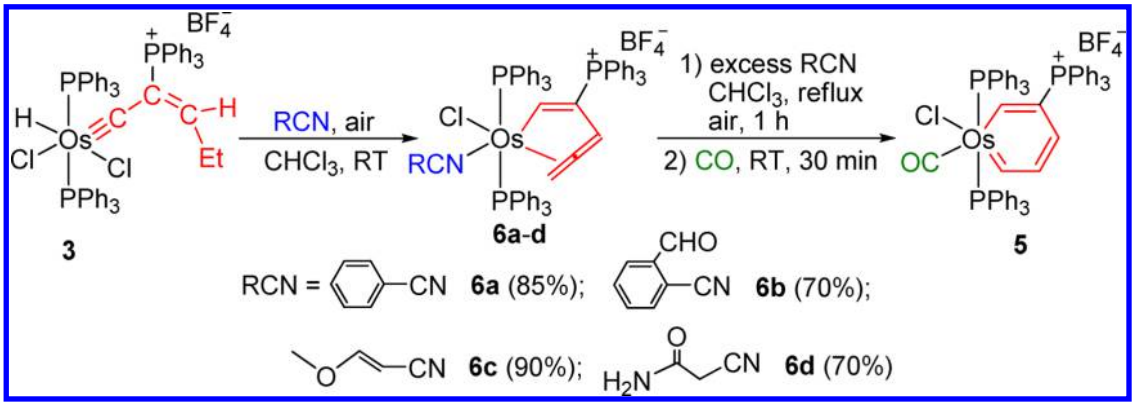
Scheme 3. Trapping of Intermediate 6



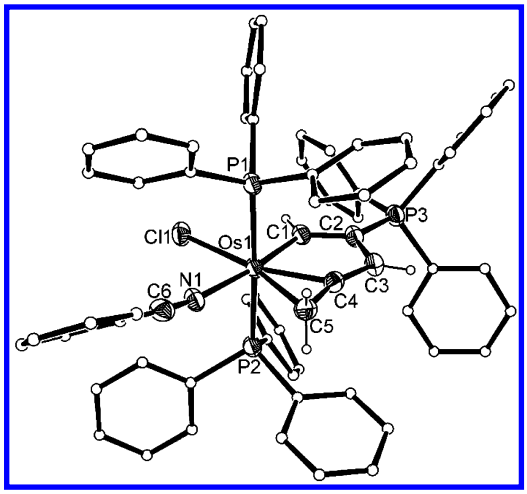
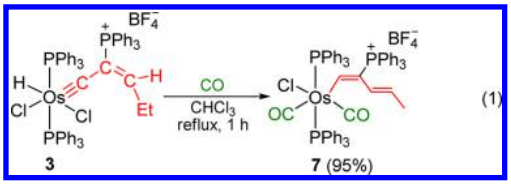


Figure 5. Molecular structure for compound **6a** (50% probability ellipsoids). The counteranion and hydrogen atoms in phenyl groups are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1−C1 = 2.050(3), Os1−C4 = 2.076(3), Os1−C5 = 2.227(3), C1−C2 = 1.362(5), C2−C3 = 1.466(5), C3−C4 = 1.332(5), C4−C5 = 1.379(5); C1−Os1−C4 = 73.00(14), C1−Os1−C5 = 110.14(14), C4−Os1−C5 = 37.16(13), C2−C1−Os1 = 121.2(3), C1−C2−C3 = 112.6(3), C4−C3−C2 = 110.4(3), C3−C4−C5 = 159.8(4).

with a relatively stronger ligand. Indeed, when excess CO was added to a $CHCl_3$ solution of **3**, it completely converted to the complex **7** in 1 h without any detectable amount of metallabenzene product, as suggested by in situ NMR (eq 1).



The structure of **7** has been determined by X-ray crystallography. A view of the complex is shown in Figure 6. The X-ray diffraction study confirms that the complex contains an unsaturated pentadienyl group. The ^{1}H NMR and ^{13}C NMR spectra of **7** are consistent with the presence of a pentadienyl ligand in the complex. In the ^{1}H NMR spectrum, this ligand exhibits resonances at 9.5 (Os*CH*), 6.0 ($CPPh_3CH$), 5.0 ($CHCH_3$), and 1.3 (CH_3) ppm. The C(sp^2) resonances in the ^{13}C NMR spectrum appear at 192.0 (C1), 120.3 (C2), 132.5 (C3), and 133.0 (C4) ppm.

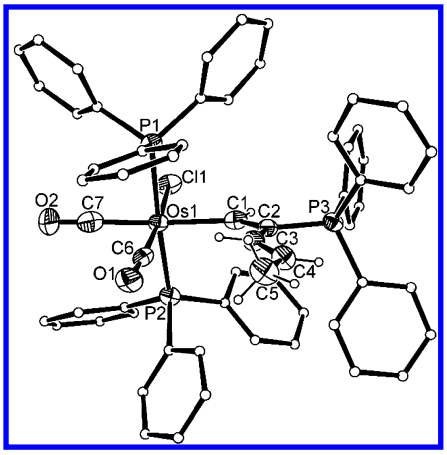


Figure 6. Molecular structure for compound **7** (50% probability ellipsoids). The counteranion and hydrogen atoms in PPh_3 groups are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1−C1 = 2.139(5), Os1−C6 = 1.921(7), C1−C2 = 1.349(7), C2−C3 = 1.478(7), C3−C4 = 1.326(7), C4−C5 = 1.485(8); Os1−C1−C2 = 133.9(4), C1−C2−C3 = 124.5(5), C2−C3−C4 = 129.3(5), C3−C4−C5 = 124.5(5).

On the basis of all of our experimental observations, we postulate the reaction mechanism shown in Scheme 4 for the formation of the metallabenzene **5** from the hydrido−butenylcarbyne complex **3** via the key intermediate **6**. A 1,2-hydrogen shift from the osmium to the carbyne carbon atom of the hydrido−butenylcarbyne complex **3** results in the formation of the butenylcarbene intermediate **A**. The whole process of hydrido−alkenylcarbyne to alkenylcarbene transformation and the influence of the coligands on the activation parameters of the 1,2-hydrogen shift have been thoroughly investigated by Esteruelas et al.[9,11] Subsequent deprotonation and coordination of one nitrile or carbonyl ligand to the metal center generate the agostic intermediate **B**. The loss of H from the pendant ethyl group may be attributed to the weak C−H bond of the allylic group. Then, dissociation of the nitrile ligand followed by hydrogen migration from the olefinic carbon atom to the metal center affords the hydrido osmacyclopentadiene intermediate **C**. **C** may undergo β-H elimination to give the η^2-allene-coordinated osmium complexes **6** in the presence of excess nitriles in an air atmosphere. Finally, the isomerization of allene complex **6** yields the unstable metallabenzene **4**, which can be easily substituted by a carbonyl ligand to give the metallabenzene **5**. The formation of metallabenzene from an η^2-allene-coordinated complex has been previously reported,[10,12]

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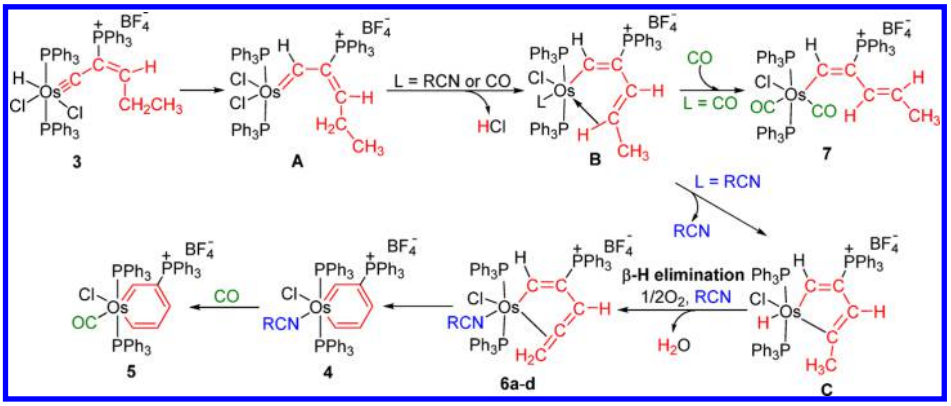
Scheme 4. Proposed Mechanism for the Conversion of 3 to 5 and 7



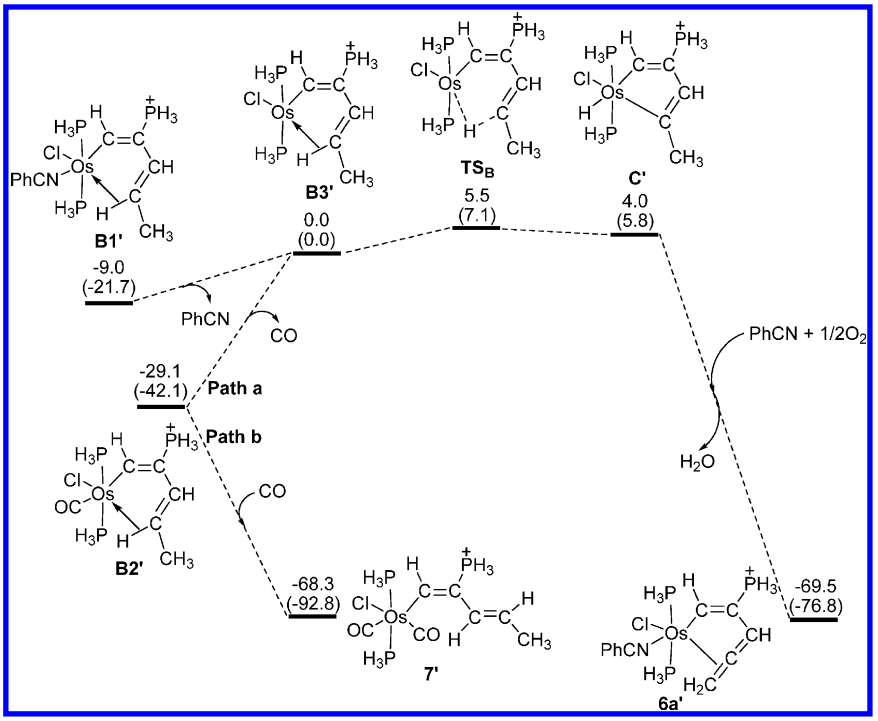


Figure 7. Energy profile calculated for the formation of 7′ and **6a**′ from intermediates **B**′ on the basis of the reaction mechanism shown in Scheme 4. The solvation-corrected relative free energies and electronic energies (in parentheses) are given in kcal/mol.

and DFT calculations were also performed to elucidate the mechanism.[10] In the presence of carbon monoxide, the propenylvinyl complex **7** was exclusively formed (**3** → **A** → **B** → **7**).

DFT Studies. To understand how the coligands influence the conversion of the hydrido−butenylcarbyne complex **3** to metallabenzene **4**, we have calculated the thermodynamics and kinetics of the key steps for the conversions of intermediates **B** to metallabenzene **4** or the propenylvinyl complex **7**. Figure 7 gives the energy profile calculated on the basis of the mechanism shown in Scheme 4, and the labels of the model compounds are followed by a prime symbol (′) to differentiate them from their corresponding experimental compounds. The theoretical calculations reproduced the conversion trend observed experimentally. As shown in Figure 7, from the benzonitrile ligand coordinated intermediate **B1**′, dissociation of the nitrile ligand proceeds to form intermediate **B3**′. The hydrogen migration occurs directly from **B3**′ via $\mathbf{TS_B}$ to give intermediate **C**′, which can further convert to the relatively more stable η^2-allene-coordinated osmium complex **6a**′. Remarkably, the free energy barrier for the conversion is as low as 14.5 kcal/mol, corresponding to the energy of $\mathbf{TS_B}$ relative to **B1**′. From the carbonyl ligand coordinated **B2**′, there are two possible paths, i.e. paths **a** and **b**, leading to the formation of the η^2-allene-coordinated osmium complex **6a**′ and the propenylvinyl complex 7′ (observed exclusively in the reaction with CO), respectively. In path **a**, the free energy barrier for the conversion is calculated to be 34.6 kcal/mol (the energy of $\mathbf{TS_B}$ relative to **B2**′). In path **b**, coordination of another carbonyl ligand generates the propenylvinyl complex 7′. Figure 7 shows that path **b** is much more favorable than path **a**. The significantly high barrier for the conversion of **B2**′ to **6a**′ is also in agreement with the experimental observation that only the propenylvinyl complex **7** can be detected in the absence of nitrile (eq 1).

A plausible explanation for the difference in the conversions is elucidated as follows. The lability of the nitrile ligand makes it easy to dissociate from the metal center, which offers an

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opportunity for further hydrogen migration, while the strong carbonyl ligand may prevent the dissociation to give the corresponding intermediate. Indeed, the calculation shows that the estimation of the free energy difference between the benzonitrile ligand coordinated intermediate **B1′** and the carbonyl ligand coordinated intermediate **B2′** to be 20.1 kcal/mol (Figure 7). This causes an increase of the barrier for the conversion of **B2′** to **6a′**. While the hydrido−butenylcarbyne to metallabenzene transformation is inhibited by the carbonyl ligand, it can be favored by the nitrile ligand. The argument can reasonably explain the experimental failure of **3** to rearrange to the corresponding metallabenzene complex without nitrile.

CONCLUSION

In summary, we have presented the synthesis of the hydrido−alkenylvinylidene complex $Os(PPh_3)_2HCl_2(=C=C(PPh_3)$-$CH=CHCH_3)$ (**2**) and hydrido−butenylcarbyne complex $[OsHCl_2(\equiv CC(PPh_3)=CH(Et))(PPh_3)_2]BF_4$ (**3**) starting from the readily accessible $HC\equiv CCH(OH)Et$ and the complex $OsCl_2(PPh_3)_3$. It is worth noting that hydrido−butenylcarbyne complex **3** can convert to metallabenzene via triple hydrogen eliminations. This conversion has been studied experimentally and computationally. All of the investigations (i.e., in situ NMR experiments and the isolation of the key intermediates) support that the conversion involves a sequence of five key steps: a 1,2-hydrogen shift, deprotonation, hydrogen migration, β-H elimination, and isomerization. With the aid of DFT calculations and further experimental proof, we demonstrated that the lability of the nitrile ligand is crucial for the conversion of the complex **3** into metallabenzene.

EXPERIMENTAL SECTION

General Methods. All manipulations were carried out under an inert atmosphere (N_2) by means of standard Schlenk techniques, unless otherwise stated. Solvents were distilled from sodium/benzophenone (tetrahydrofuran, Et_2O) or calcium hydride (CH_2Cl_2) under N_2 prior to use. Other reagents were used as received from commercial sources without further purification. NMR spectroscopic experiments were carried out on a Bruker AVIII-500 spectrometer (^1H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{31}P, 202.5 MHz), Bruker AV-400 spectrometer (^1H, 400.1 MHz; ^{13}C, 100.2 MHz; ^{31}P, 162.0 MHz). ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. Elemental analyses were performed on a Vario EL III elemental analyzer. High-resolution mass spectrometry (HRMS) experiments were performed on a Bruker En Apex Ultra 7.0T FT-MS.

Synthesis of $(PPh_3)_2Cl_2Os(CHC(PPh_3)CH(OH)CH_2CH_3)$ (1). $HC\equiv CCH(OH)Et$ (0.43 mL, 4.97 mmol) was added to a solution of $OsCl_2(PPh_3)_3$ (4.00 g, 3.82 mmol) in tetrahydrofuran (20 mL). The reaction mixture was stirred at room temperature for 3 h to give a yellow suspension. The yellow solid was collected by filtration, washed with Et_2O (4 × 30 mL) and dried in vacuo. Yield: 2.59 g, 60%. ^1H NMR (500 MHz, CD_2Cl_2): δ 12.1 (br, 1 H, C^1H), 2.9 (br, 1 H, C^3H), 2.4 (br, 1 H, O*H*), 0.9 (br, 1 H, C^4H), 0.3 (br, 3 H, C^5H), 7.6−6.8 ppm (m, 45 H, PPh_3). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 3.1 (br, C*P*Ph_3), 6.3 (br, Os*P*Ph_3), −3.1 ppm (br, Os*P*Ph_3). ^{13}C NMR plus $^1H-^{13}C$ HSQC (125 MHz, CD_2Cl_2): δ 207.1 (br, C^1), 104.3 (d, $^1J(PC)$ = 79.1 Hz, C^2), 85.5 (d, $^2J(PC)$ = 31.5 Hz, C^3), 30.9 (br, C^4), 10.5 (s, C^5), 122.2−138.6 ppm (m, PPh_3). Anal. Calcd for $C_{59}H_{53}OCl_2P_3Os$: C, 62.59; H, 4.72. Found: C, 62.40; H, 5.07.

Synthesis of $Os(PPh_3)_2HCl_2(=C=C(PPh_3)CH=CHCH_3)$ (2). A mixture of **1** (3.00 g, 2.65 mmol) and excess P_2O_5 in CH_2Cl_2 (50 mL) was stirred under reflux for about 1 h to give a yellow solution which was collected by filtration. The filtrate was concentrated to about 1 mL under vacuum. The addition of Et_2O (20 mL) to the residue produced a yellow precipitate, which was washed with Et_2O (2 × 20 mL) and dried under vacuum. Yield: 2.07 g, 70%. ^1H NMR (500 MHz, CD_2Cl_2): δ 5.5 (m, 1 H, C^4H), 5.3 (dd, apparent t, $^3J(PH)$ = 15.5 Hz, $^3J(HH)$ = 15.5 Hz, 1 H, C^3H), 1.8 (d, $^3J(HH)$ = 6.5 Hz, 3 H, C^5H), −7.7 (td, $^2J(PH)$ = 15.5 Hz, $^4J(PH)$ = 4.5 Hz, 1 H, Os*H*), 7.5−6.4 ppm (m, 45 H, PPh_3), ^{31}P NMR (202 MHz, CD_2Cl_2): δ 7.7 (s, C*P*Ph_3), 3.7 ppm (s, Os*P*Ph_3). Anal. Calcd for $C_{59}H_{51}Cl_2P_3Os$: C, 63.61; H, 4.61. Found: C, 63.44; H, 4.60. HRMS (ESI): m/z [**2** − Cl^-]$^+$ calcd for $[C_{59}H_{51}ClOsP_3]^+$ 1079.2507, found 1079.2496.

Synthesis of $[OsHCl_2(\equiv C-C(PPh_3)=CH(Et))(PPh_3)_2]BF_4$ (3). A solution of $HBF_4{\cdot}Et_2O$ (250 μL, 0.96 mmol) was added to a suspension of compound **2** (1.00 g, 0.90 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred at room temperature for 30 min to give a brown solution. The volume of the solution was reduced to approximately 1 mL under vacuum. The addition of Et_2O (20 mL) to the residue produced a gray precipitate, which was collected by filtration, washed with Et_2O (2 × 20 mL), and dried under vacuum. Yield: 1.06 g, 98%. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.3 (m, 1 H, C^3H), 3.2 (m, 2 H, C^4H), 1.3 (t, $^3J(HH)$ = 7 Hz, 3 H, C^5H), −5.18 (td, $^2J(PH)$ = 16.6 Hz, $^4J(PH)$ = 3.0 Hz, 1 H, Os*H*), 7.7−7.2 ppm (m, 45 H, PPh_3). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 15.9 (s, C*P*Ph_3), 3.9 ppm (s, Os*P*Ph_3). Anal. Calcd for $C_{59}H_{52}Cl_2P_3BF_4Os$: C, 58.96; H, 4.36. Found: C, 59.30; H, 4.67.

Synthesis of $[(PPh_3)_2(CO)ClOs(CHC(PPh_3)CHCHCH)]BF_4$ (5). *Method A.* Benzonitrile (0.65 mL, 6.3 mmol) was added to a suspension of **3** (500 mg, 0.42 mmol) in $CHCl_3$ (10 mL). The reaction mixture was stirred under reflux for about 1 h to give a brown solution in air. Then a continuous flow of CO was bubbled into the solution, which was further stirred for 0.5 h at room temperature to give a brown solution. The volume of the mixture was reduced to approximately 1 mL under vacuum. The residues were purified by column chromatography (neutral alumina, eluent CH_2Cl_2/acetone 10/1) to give **5** as a purple solid. Yield: 150 mg, 30%. Complex **5** could also be prepared by the reactions of complex **3** with 2-cyanobenzaldehyde, 3-methoxyacrylonitrile, and 2-cyanoacetamide under the same conditions in 29%, 33%, and 26% yields, respectively.

Method B. Benzonitrile (0.60 mL, 5.8 mmol) was added to a solution of **6a** (500 mg, 0.39 mmol) in $CHCl_3$ (10 mL). The reaction mixture was stirred under reflux for about 1 h in air. Then a continuous flow of CO was bubbled into the solution, which was further stirred for 0.5 h at room temperature to give a brown solution. Then the volume of the mixture was reduced to approximately 1 mL under vacuum. The residue was purified by column chromatography (neutral alumina, eluent CH_2Cl_2/acetone 10/1) to give **5** as a purple solid. Yield: 186 mg, 40%. Complex **5** could also be prepared by the reaction of complexes (**6b−d**) with their corresponding nitriles (2-cyanobenzaldehyde, 3-methoxyacrylonitrile, and 2-cyanoacetamide) under the same conditions in 34%, 42%, and 33% yields, respectively. ^1H NMR (500 MHz, CD_2Cl_2): δ 15.9 (d, $^3J(HH)$ = 8.0 Hz, 1 H, C^5H), 13.1 (d, $^3J(PH)$ = 29.5 Hz, 1 H, C^1H), 7.9−7.0 ppm (m, 47 H, C^3H, C^4H, and PPh_3). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 18.6 (s, C*P*Ph_3), −2.9 ppm (s, Os*P*Ph_3). ^{13}C NMR (125.8 MHz, CD_2Cl_2, plus $^1H-^{13}C$ HSQC, $^1H-^{13}C$ HMQC, and dept-135): δ 261.6 (br, C^5), 234.0 (br, C^1), 190.7 (m, C^6), 141.8 (d, $^2J(PC)$ = 21.3 Hz, C^3), 114.4 (d, $^1J(PC)$ = 72.5 Hz, C^2), 135.5−120.0 ppm (m, C^4 and PPh_3). Anal. Calcd for $C_{60}H_{49}ClOP_3BF_4Os$: C, 60.48; H, 4.15. Found: C, 60.34; H, 4.32. HRMS (ESI): m/z $[M]^+$ calcd for $[C_{60}H_{49}ClOOsP_3]^+$ 1105.2288, found 1105.2287.

Synthesis of $[(PPh_3)_2(CO)ClOs(CHC(PPh_3)CHCHCH)]BPh_4$ (5′). $NaBPh_4$ (170 mg, 0.50 mmol) was added to a solution of **5** (500 mg, 0.42 mmol) in CH_3OH (10 mL). The reaction mixture was stirred for about 5 min to give a purple precipitate, which was collected by filtration, washed with CH_3OH (2 × 2 mL) and Et_2O (3 × 10 mL), and then dried under vacuum. Yield: 569 mg, 95%. ^1H NMR (500 MHz, CD_2Cl_2): δ 15.8 (d, $^3J(HH)$ = 8.0 Hz, 1 H, C^5H), 13.0 (d, $^3J(PH)$ = 29.5 Hz, 1 H, C^1H), 7.7−6.7 ppm (m, 67 H, other hydrogens). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 18.6 (s, C*P*Ph_3), −2.6 ppm (s, Os*P*Ph_3). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 261.6 (br, C^5), 234.1 (br, C^1), 190.7 (m, C^6), 141.7 (d, $^2J(PC)$ = 21.3 Hz, C^3), 114.3 (d, $^1J(PC)$ = 72.5 Hz, C^2), 136.0−119.4 (m, C^4 and PPh_3), 164.7−

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163.5 ppm (m, BPh_4). Anal. Calcd for $C_{84}H_{69}ClOP_3BOs$: C, 70.86; H, 4.88. Found: C, 70.42; H, 4.88.

Synthesis of $[(PPh_3)_2(PhCN)ClOs(CHC(PPh_3)CHCCH_2)]BF_4$ (6a). Benzonitrile (89 μL, 0.84 mmol) was added to a suspension of **3** (500 mg, 0.42 mmol) in $CHCl_3$ (10 mL). The reaction mixture was stirred at room temperature for 5 h in air and was then concentrated to about 1 mL under vacuum. The addition of Et_2O (20 mL) to the residue produced a yellow precipitate, which was collected by filtration, washed with Et_2O (2 × 10 mL), and dried under vacuum. Yield: 448 mg, 85%. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 11.5 (d, ^3J(PH) = 16.5 Hz, 1 H, C^1H), 7.6 ppm (br, 1 H, C^3H, obscured by the phenyl signals and confirmed by ^{1}H−^{13}C HMBC), 2.8 (t, ^3J(PH) = 6.2 Hz, 2 H, C^5H), 7.8−7.0 ppm (m, 51 H, PPh_3 and Ph). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 8.8 (s, CPPh$_3$), −9.9 ppm (s, OsPPh$_3$), ^{13}C NMR (125 MHz, CD_2Cl_2): δ 203.4 (t, ^2J(PC) = 7.9 Hz, C^1), 190.3 (d, ^3J(PC) = 22.1 Hz, C^4), 120.9 (d, ^1J(PC) = 82.0 Hz, C^2), 116.8 (d, ^2J(PC) = 26.3 Hz, C^3), 110.7 (s, PhCN), 26.0 (s, C^5) 134.2−127.6 ppm (m, other carbons). Anal. Calcd for $C_{66}H_{54}ClNP_3BF_4Os$: C, 62.59; H, 4.30; N, 1.11. Found: C, 62.50; H, 4.29; N, 0.99. HRMS (ESI): m/z [M − PhCN]$^+$ calcd for $[C_{59}H_{49}ClOsP_3]^+$ 1077.2350, found 1077.2349.

Synthesis of $[(PPh_3)_2(PhCOH(2\text{-}CN))ClOs(CHC(PPh_3)CHCCH_2)]BF_4$ (6b). A mixture of **3** (500 mg, 0.42 mmol) and 2-cyanobenzaldehyde (108 mg, 0.84 mmol) in $CHCl_3$ (10 mL) was stirred at room temperature for 4 h in air to give a yellow solution. The solvent was removed under vacuum and concentrated to about 1 mL under vacuum. The addition of Et_2O (20 mL) to the residue produced a yellow precipitate, which was collected by filtration, washed with Et_2O (2 × 10 mL), and dried under vacuum. Yield: 377 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.6 (d, ^3J(PH) = 16.3 Hz, 1 H, C^1H), 9.8 (s, 1 H, PhCOH(2-CN)), 3.4 (br, 2 H, C^{5}H), 8.1−7.0 ppm (m, 50 H, PPh_3, Ph, and C^3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 9.1 (s, CPPh$_3$), −10.1 ppm (s, OsPPh$_3$). ^{13}C NMR (100 MHz, CD_2Cl_2, plus ^{1}H−^{13}C HSQC, ^{1}H−^{13}C HMQC, and dept-135): δ 202.6 (br, C^1), 190.7 (br, C^4), 188.8 (s, PhCOH(2-CN)). 137.0 (s, PhCOH(2-CN)), 120.9 (d, J(PC) = 88.0 Hz, C^2), 116.5 (d, ^3J(PC) = 26.8 Hz, C^3), 24.2 (s, C^5), 135.5−127.5 ppm (m, other aromatic carbons). Anal. Calcd for $C_{67}H_{54}ClNOP_3BF_4Os$: C, 62.16; H, 4.20; N, 1.08. Found: C, 62.33; H, 4.46; N, 1.02. HRMS (ESI): m/z [M − C_8H_5NO]$^+$ calcd for $[C_{59}H_{49}ClP_3Os]^+$ 1077.2350, found 1077.2335.

Synthesis of $[(PPh_3)_2(CH_3OCHCHCN)ClOs(CHC(PPh_3)CHCCH_2)]BF_4$ (6c). 3-Methoxyacrylonitrile (64 μL, 0.84 mmol) was added to a suspension of **3** (500 mg, 0.42 mmol) in $CHCl_3$ (10 mL). The mixture was stirred at room temperature for 3 h in air. The reaction mixture was concentrated to about 1 mL under vacuum. The addition of Et_2O (20 mL) to the residue produced a yellow precipitate, which was collected by filtration, washed with Et_2O (2 × 10 mL), and dried under vacuum. Yield: 467 mg, 90%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 11.4 (d, ^3J(PH) = 16.6 Hz, 1 H, C^1H), 6.9 (d, ^3J(HH) = 12.8 Hz, 1 H, CH_3OCH), 4.6 (d, ^3J(HH) = 12.8 Hz, 1 H, CH_3OCHCH), 3.6 (s, 3 H, CH_3O), 2.7 (br, 2 H, C^5H), 7.7−6.9 ppm (m, 46 H, PPh_3 and C^3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.5 (s, CPPh$_3$), −10.2 ppm (s, OsPPh$_3$), ^{13}C NMR (100 MHz, CD_2Cl_2, plus ^{1}H−^{13}C HSQC, ^{1}H−^{13}C HMQC, and dept-135): δ 203.9 (t, ^2J(PC) = 9.9 Hz, C^1), 190.6 (d, ^3J(PC) = 28.3 Hz, C^4), 168.1 (s, CH_3OCH), 125.5 (s, $CH_3OCHCHCN$), 120.9 (d, ^1J(PC) = 110.4 Hz, C^2), 116.5 (d, ^2J(PC) = 33.0 Hz, C^3), 74.0 (s, CH_3OCHCH), 58.7 (s, CH_3O), 24.8 (s, C^5), 134.0−127.5 ppm (m, PPh_3). Anal. Calcd for $C_{63}H_{54}ClNOP_3BF_4Os$: C, 60.70; H, 4.37; N, 1.12. Found: C, 60.62; H, 4.46; N, 1.12. HRMS (ESI): m/z [M − $CH_3OCH{=}CHCN$]$^+$ calcd for $[C_{59}H_{49}ClOsP_3]^+$ 1077.2350, found 1077.2362.

Synthesis of $[(PPh_3)_2(NH_2COCH_2CN)ClOs(CHC(PPh_3)CHCCH_2)]BF_4$ (6d). A mixture of **3** (500 mg, 0.42 mmol) and 2-cyanoacetamide (82 mg, 0.84 mmol) in $CHCl_3$ (10 mL) was stirred at room temperature for 16 h in air. The reaction mixture was concentrated to about 1 mL under vacuum. The addition of Et_2O (20 mL) to the residue produced a yellow precipitate, which was collected by filtration, washed with Et_2O (2 × 10 mL), and dried under vacuum. Yield: 364 mg, 70%. ^{1}H NMR (500 MHz, CD_3CN): δ 11.3 (d, ^3J(PH) = 15.4 Hz, 1 H, C^1H), 6.3 (s, 1 H, NH_2), 5.9 (s, 1 H, NH_2), 3.4 (s, 2 H, NH_2COCH_2), 2.5 (br, 2 H, C^5H), 7.7−6.9 ppm (m, PPh_3 and C^3H). ^{31}P NMR (202 MHz, CD_3CN): δ 8.7 (s, CPPh$_3$), −10.0 ppm (s, OsPPh$_3$), ^{13}C NMR (125 MHz, CD_3CN, plus ^{1}H−^{13}C HSQC, ^{1}H−^{13}C HMQC and dept-135): δ 203.3 (t, ^2J(PC) = 7.5 Hz, C^1), 190.0 (d, ^3J(PC) = 22.4 Hz, C^4), 164.0 (s, NH_2CO), 120.8 (d, ^1J(PC) = 75.3 Hz, C^2), 116.8 (d, ^2J(PC) = 26.2 Hz, C^3), 115.3 (s, NH_2COCH_2CN), 25.3 (s, NH_2COCH_2), 24.6 (s, C^5), 134.2−127.5 ppm (m, PPh_3). Anal. Calcd for $C_{62}H_{53}ClN_2OP_3BF_4Os$: C, 59.69; H, 4.28; N, 2.25. Found: C, 59.57; H, 4.10; N, 2.42. HRMS (ESI): m/z [M − H_2NCOCH_2CN]$^+$ calcd for $[C_{59}H_{49}ClOsP_3]^+$ 1077.2350, found 1077.2355.

Synthesis of $[(PPh_3)_2(CO)_2ClOs(CHC(PPh_3)CHCHCH_3)]BF_4$ (7). A suspension of **3** (500 mg, 0.42 mmol) in $CHCl_3$ (10 mL) was refluxed for 1 h in carbon monoxide. The reaction mixture was concentrated to about 1 mL under vacuum at room temperature. The addition of Et_2O (20 mL) to the residue produced a white precipitate, which was collected by filtration, washed with Et_2O (2 × 10 mL), and dried under vacuum. Yield: 482 mg, 95%. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 9.5 (d, ^3J(PH) = 35.4 Hz, 1 H, C^1H), 6.0 (m, 1 H, C^3H), 5.0 (m, 1 H, C^4H), 1.3 (br, 3 H, C^5H), 7.7−6.9 ppm (m, 45 H, PPh_3). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 18.4 (t, ^4J(PP) = 5.3 Hz, CPPh$_3$), −12.1 ppm (d, ^4J(PP) = 5.3 Hz, OsPPh$_3$). ^{13}C NMR (125 MHz, CD_2Cl_2, plus ^{1}H−^{13}C HMQC): δ 192.0 (t, ^2J(PC) = 11.1 Hz, C^1), 179.9 (dd, ^4J(PC) = 16.7 Hz, ^2J(PC) = 7.8 Hz, CO), 175.8 (t, ^2J(PC) = 7.3 Hz, CO), 132.5 (d, ^2J(PC) = 18.6 Hz, C^3), 133.0 (s, C4), 120.3 (d, ^1J(PC) = 85.5 Hz, C^2), 18.5 (s, C^5), 134.7−128.1 ppm (m, PPh_3). Anal. Calcd for $C_{61}H_{51}ClO_2P_3BF_4Os$: C, 59.98; H, 4.21. Found: C, 60.34; H, 4.32.

Crystallographic Analysis. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 solutions layered with hexane for **1**−**3**, **5**′, **6a**, and **7**. Data collections were performed on an Oxford Gemini S Ultra or a Rigaku R-AXIS SPIDER IP CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Multiscan absorption corrections (SADABS) were applied. All of the data were corrected for absorption effects using the multiscan technique. The structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least squares on F^2 using the Bruker SHELXTL (version 6.10) program package. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. CCDC 939766 (**1**), 939767 (**2**), 939768 (**3**), 939769 (**5**′), 939770 (**6a**), and 939772 (**7**) contain the supplementary crystallographic data for this paper. Further details on crystal data, data collection, and refinements are summarized in Table S1 (Supporting Information).

Computational Details. Molecular geometries of the reactants, intermediates, transition states, and products were optimized via density functional theory calculations using the hybrid Becke3LYP (B3LYP) method.[13] The 6-31g** basis set was used for the C, O, N, and H atoms, while the effective core potentials (ECPs) of Hay and Wadt with double-ζ valence basis set (LanL2DZ)[14] were chosen to describe the Os, P, and Cl atoms. In addition, polarization functions were added for Os(ζf) = 0.886, P(ζd) = 0.340, and Cl(ζd) = 0.514.[15] Frequency analyses have been performed to obtain the zero-point energies (ZPE) and identify all of the stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency) on the potential energy surfaces (PES). Intrinsic reaction coordinate (IRC) calculations were also calculated for the transition states to confirm that such structures indeed connect two relevant minima.[16] To reduce the computational cost, the PPh_3 group was modeled by PH_3. All calculations were performed with the Gaussian 03 software package.[17]

To consider solvent effects, a continuum medium was employed to do single-point energy calculations for all of the optimized species, using UAHF radii on the conductor-like polarizable continuum model (CPCM).[18] Chloroform was used as the solvent, according to the experimental reaction conditions.

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■ ASSOCIATED CONTENT

Supporting Information

Tables giving Cartesian coordinates for all of the calculated structures and CIF files and a table giving crystallographic data of compounds **1**−**3**, **5′**, **6a**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org..

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For recent reviews, see: (a) Shi, C.; Jia, G. *Coord. Chem. Rev.* **2013**, *257*, 666. (b) Bezuidenhout, D. I.; Lotz, S.; Liles, D. C.; van der Westhuizen, B. *Coord. Chem. Rev.* **2012**, *256*, 479. (c) Takemoto, S.; Matsuzaka, H. *Coord. Chem. Rev.* **2012**, *256*, 574. (d) Herndon, J. W. *Coord. Chem. Rev.* **2011**, *255*, 3. (e) Werner, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 4714. (f) Herndon, J. W. *Coord. Chem. Rev.* **2010**, *254*, 103. (g) Conejero, S.; Paneque, M.; Poveda, M. L.; Santos, L. L.; Carmona, E. *Acc. Chem. Res.* **2010**, *43*, 572. (h) Rosenberg, L. *Coord. Chem. Rev.* **2012**, *256*, 606.

(2) For recent reviews, see: (a) Zhu, C. Q.; Cao, X. Y.; Xia, H. P. *Chin. J. Org. Chem.* **2013**, *33*, 657. (b) Chen, J.; Jia, G. *Coord. Chem. Rev.* **2013**, DOI: 10.1016/j.ccr.2013.01.014. (c) Paneque, M.; Poveda, M. L.; Rendón, N. *Eur. J. Inorg. Chem.* **2011**, 19. (d) Bleeke, J. R. *Acc. Chem. Res.* **2007**, *40*, 1035. (e) Wright, L. J. *Dalton Trans.* **2006**, *15*, 1821. (f) Landorf, C. W.; Haley, M. M. *Angew. Chem.* **2006**, *118*, 4018; *Angew. Chem., Int. Ed.* **2006**, *45*, 3914. (g) Jia, G. *Acc. Chem. Res.* **2004**, *37*, 479. (h) He, G. M.; Xia, H. P.; Jia, G. C. *Chin. Sci. Bull.* **2004**, *49*, 1543. (i) Bleeke, J. R. *Chem. Rev.* **2001**, *101*, 1205.

(3) Recent examples for the synthesis of metallabenzenes from the reactions of simple transition-metal complexes with unsaturated hydrocarbons: (a) Gong, L.; Lin, Y.; Wen, T. B.; Xia, H. *Organometallics* **2009**, *28*, 1101. (b) Jacob, V.; Landorf, C. W.; Zakharov, L. N.; Weakley, T. J. R.; Haley, M. M. *Organometallics* **2009**, *28*, 5183. (c) Zhang, H.; Wu, L.; Lin, R.; Zhao, Q.; He, G.; Yang, F.; Wen, T. B.; Xia, H. *Chem. Eur. J.* **2009**, *15*, 3546.

(4) Recent examples for the synthesis of metallabenzenes from the conversions of various unsaturated metallacycles: (a) Hernández-Juárez, M.; Salazar, V.; García-Báez, E. V.; Padilla-Marínez, I. I.; Höpfl, H.; Rosales-Hoz, M. d. J. *Organometallics* **2012**, *31*, 5438. (b) Paneque, M.; Poveda, M. L.; Rendon, N. *Eur. J. Inorg. Chem.* **2011**, *1*, 19. (c) Poon, K. C.; Liu, L.; Guo, T.; Li, J.; Sung, H. H. Y.; Williams, I. D.; Lin, Z.; Jia, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 2759. (d) Huang, J. B.; Lin, R.; Wu, L. Q.; Zhao, Q. Y.; Zhu, C. Q.; Wen, T. B.; Xia, H. P. *Organometallics* **2010**, *29*, 2916. (e) Clark, G. R.; Ferguson, L. A.; McIntosh, A. E.; Sohnel, T.; Wright, L. J. *J. Am. Chem. Soc.* **2010**, *132*, 13443. (f) Clark, G. R.; O'Neale, T. R.; Roper, W. R.; Tonei, D. M.; Wright, L. J. *Organometallics* **2009**, *28*, 567. (g) Dalebrook, A. F.; Wright, L. J. *Organometallics* **2009**, *28*, 5536.

(5) (a) Liu, B.; Zhao, Q. Y.; Wang, H. J.; Chen, J. X.; Cao, X. Y.; Cao, Z. X.; Xia, H. P. *Chin. J. Chem.* **2012**, *30*, 2158. (b) Liu, B.; Wang, H.; Xie, H.; Zeng, B.; Chen, J.; Tao, J.; Wen, T. B.; Cao, Z.; Xia, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 5430. (c) Liu, B.; Xie, H.; Wang, H.; Wu, L.; Zhao, Q.; Chen, J.; Wen, T. B.; Cao, Z.; Xia, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 5461.

(6) Recent examples of osmium−vinylidene complexes: (a) Zhao, Q.; Cao, X. Y.; Wen, T. B.; Xia, H. *Chem. Asian J.* **2013**, *8*, 269. (b) Esteruelas, M. A.; Lopez, A. M.; Mora, M.; Onate, E. *Organometallics* **2012**, *31*, 2965. (c) Buil, M. L.; Esteruelas, M. A.; Garces, K.; Onate, E. *J. Am. Chem. Soc.* **2011**, *133*, 2250. (d) Batuecas, M.; Escalante, L.; Esteruelas, M. A.; García-Yebra, C.; Oñate, E.; Saá, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 9712. (e) Castro-Rodrigo, R.; Esteruelas, M. A.; Lopez, A. M.; Mozo, S.; Onate, E. *Organometallics* **2010**, *29*, 4071. (f) Castro-Rodrigo, R.; Esteruelas, M. A.; Lopez, A. M.; Lopez, F.; Mascarenas, J. L.; Olivan, M.; Onate, E.; Saya, L.; Villarino, L. *J. Am. Chem. Soc.* **2010**, *132*, 454. (g) Richter, B.; Werner, H. *Eur. J. Inorg. Chem.* **2009**, *31*, 4625. (h) Huang, D.; Olivan, M.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 4700. (i) Lee, J.-H.; Pink, M.; Caulton, K. G. *Organometallics* **2006**, *25*, 802.

(7) Jia, G. *Coord. Chem. Rev.* **2007**, *251*, 2167.

(8) Recent examples of alkenylcarbyne complexes: (a) Chen, J.; Shi, C.; Sung, H. H.-Y.; Williams, I. D.; Lin, Z.; Jia, G. *Organometallics* **2012**, *31*, 1817. (b) Chen, J.; Shi, C.; Sung, H. H.-Y.; Williams, I. D.; Lin, Z.; Jia, G. *Chem. Eur. J.* **2012**, *18*, 14128. (c) Hudson, D. M.; Valente, E. J.; Schachner, J.; Limbach, M.; Muller, K.; Schanz, H.-J. *ChemCatChem* **2011**, *3*, 297. (d) Collado, A.; Esteruelas, M. A.; Onate, E. *Organometallics* **2011**, *30*, 1930. (e) Chen, J.; Sung, H. H.-Y.; Williams, I. D.; Jia, G. *Organometallics* **2011**, *30*, 6159. (f) Chen, J.; He, G.; Sung, H. H.-Y.; Williams, I. D.; Lin, Z.; Jia, G. *Organometallics* **2010**, *29*, 2693. (g) Castro-Rodrigo, R.; Esteruelas, M. A.; Lopez, A. M.; Mozo, S.; Onate, E. *Organometallics* **2010**, *29*, 4071.

(9) Bolano, T.; Castarlenas, R.; Esteruelas, M. A.; Modrego, F. J.; Onate, E. *J. Am. Chem. Soc.* **2005**, *127*, 11184.

(10) Gong, L.; Chen, Z.; Lin, Y.; He, X.; Bin Wen, T.; Xu, X.; Xia, H. *Chem. Eur. J.* **2009**, *15*, 6258.

(11) (a) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2008**, *27*, 3547. (b) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 2037.

(12) Lin, R.; Zhao, J.; Chen, H.; Zhang, H.; Xia, H. *Chem. Asian J.* **2012**, *7*, 1915.

(13) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (d) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785.

(14) (a) Check, C. E.; Faust, T. O.; Bailey, J. M.; Wright, B. J.; Gilbert, T. M.; Sunderlin, L. S. *J. Phys. Chem. A* **2001**, *105*, 8111. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(15) Huzinaga, S., *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

(16) (a) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161. (b) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J. B.; Stefanov, B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, revision B05*; Gaussian, Inc., Pittsburgh, PA, 2003.

(18) (a) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669. (b) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.